Anal. Calcd for $C_{22}H_{22}ClIrONP$: C, 46.0; H, 3.85; N, 2.44. Found: C, 45.9; H, 3.90; N, 2.36.

Chlorocarbonylbis(*o*-(diphenylphosphino)-*N*,*N*-dimethylbenzylamine)iridium(I), $IrCl(CO)(PCN)_2$. The solution of $Li[IrCl_2(CO)_2]$ was prepared as described above using $IrCl_3 \cdot xH_2O$ (0.063 g). An excess of PCN (>2 mol) was added to the solution, which was allowed to cool. The yellow solid was filtered, washed with ethanol and then diethyl ether, and dried in vacuo; yield 0.07 g (44%); mp 220 °C. Anal. Calcd for $C_{43}H_{44}ClIrN_2OP_2$: C, 57.7; H, 4.96; N, 3.13. Found: C, 57.5; H, 4.91; N, 2.97.

Chlorocarbonylbis(*o*-(diphenylphosphino)anisole)iridium(I), $IrCl(CO)(PO)_2$. The solution of $Li[IrCl_2(CO)_2]$ was prepared using $IrCl_3 \cdot xH_2O$ (1.5 g) and LiCl (0.18 g). To this solution was added PO (2.44 g) and the hot solution allowed to cool. The yellow solid was filtered, washed with ethanol and then diethyl ether, and dried in vacuo; yield 2.72 g (77%); mp 237–240 °C dec. Anal. Calcd for $C_{39}H_{34}ClIrO_3P_2$: C, 55.8; H, 4.08. Found: C, 55.3; H, 4.36.

Hydrodichlorocarbonyl(*o*-(diphenylphosphino)-*N*,*N*-dimethylaniline)iridium(III), $IrHCl_2(CO)PN$. A suspension of IrCl(CO)PN (0.15 g) in ethanol was deoxygenated with a steady stream of nitrogen for 15 min. To the solution was added 6 M HCl (0.5 mL) and the solution stirred for 6 h under a nitrogen atmosphere. To the filtered solution was added hexane until the compound precipitated as a white solid. The compound was washed with diethyl ether and dried in air; yield 0.15 g (94%); mp 195–196 °C. Anal. Calcd for $C_{21}H_{21}Cl_2IrNPO$: C, 42.4; H, 3.52; N, 2.34. Found: C, 42.0; H, 3.45; N, 2.30.

Hydrodichlorocarbonyl(*o*-(diphenylphosphino)-*N*,*N*-dimethylbenzylamine)iridium(III), $IrHCl_2(CO)PCN$. By using a similar procedure for $IrHCl_2(CO)PN$ the compound was prepared from IrCl(CO)PCN (0.115 g); yield 0.104 g (85%); dec pt >230 °C. Anal. Calcd for $C_{22}H_{23}Cl_2IrNPO$: C, 43.2; H, 3.79; N, 2.29. Found: C, 42.9; H, 3.81; N, 2.29.

Methyldiiodocarbonyl(*o*-(diphenylphosphino)-*N*,*N*-dimethylaniline)iridium(III), $IrMeI_2(CO)PN$. A solution of IrCl(CO)PN (0.2 g) and sodium iodide (0.7 g) was stirred in methanol, saturated with carbon monoxide, for 15 min. Methyl iodide (0.18 mL) was added, and the reaction mixture stirred for 45 min. The solvent was removed on a rotary evaporator and the residue extracted with dichloromethane (30 mL). Following filtration through Celite, ethanol (60 mL) was added, and the dichloromethane slowly removed. The complex was crystallized, filtered, washed with ethanol (3 × 5 mL) and diethyl ether (2 × 10 mL), and dried in vacuo. The fawn-colored compound showed a single spot on TLC using CH_2Cl_2–$(CH_3)_2CO$ in the ratio 10:1; yield 0.2 g (71%); mp 225–230 °C dec. Anal. Calcd for $C_{22}H_{23}I_2IrNPO$: C, 33.2; H, 2.90; N, 1.76. Found: C, 32.9; H, 2.83; N, 1.77.

Methyldiiodocarbonyl(*o*-(diphenylphosphino)-*N*,*N*-dimethylbenzylamine)iridium(III), $IrMeI_2(CO)PCN$. The compound IrCl(CO)PCN (0.112 g) and sodium iodide (0.05 g) were suspended in oxygen-free acetone (20 mL). The solution was stirred for 30 min to complete the metathetical replacement. Carbon monoxide was bubbled through the solution and excess methyl iodide added. After stirring of the mixture for 30 min the volume of acetone was reduced to 1–2 mL, and hexane was added. The yellow-brown precipitate was filtered, washed with diethyl ether, and dried in air; yield 0.13 g (81%); mp >300 °C. Anal. Calcd for $C_{23}H_{25}I_2IrNPO$: C, 34.2; H, 3.12; N, 1.73. Found: C, 34.1; H, 3.20; N, 1.68.

Acknowledgment. We wish to thank the National Science Foundation for support of this work under Grant No. CHE 73-08793 A02. S.F.A. acknowledges support as a National Science Foundation undergraduate research participant. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We thank Dr. J. A. Magnuson for use of the DNMR-3 computer program.

Registry No. IrCl(CO)PN, 61483-21-4; IrCl(CO)PCN, 61483-22-5; $IrCl(CO)(PCN)_2$, 61483-23-6; $IrCl(CO)(PO)_2$, 61483-24-7; $IrHCl_2(CO)PN$, 61483-25-8; $IrHCl_2(CO)(PCN)$, 61483-26-9; $IrMeI_2(CO)(PN)$, 61483-20-3; $IrMeI_2(CO)(PCN)$, 61505-83-7; RhCl(CO)PCN, 53897-08-8; $Li[IrCl_2(CO)_2]$, 55095-92-6; PN, 4358-50-3; PCN, 53881-33-7; PO, 53111-20-9.

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Contribution from the Department of Chemistry,
University of California, Davis, California 95616

Preparation and Dynamic Properties of Some Dimeric Palladium(I) and Platinum(I) Complexes

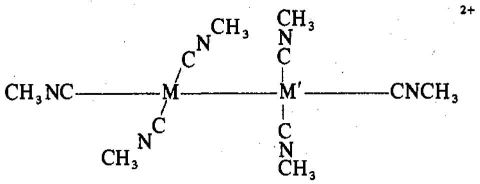
JOHN R. BOEHM and ALAN L. BALCH*

Received July 14, 1976 AIC60508K

Substitution reactions of the dimers $[Pd_2(CNCH_3)_6](PF_6)_2$, **1**, $[Pt_2(CNCH_3)_6](BF_4)_2$, **2**, and $[PdPt(CNCH_3)_6](PF_6)_2$, **3**, are described. Exchange of **1** or **2** with free methyl isocyanide is fast on a ^1H NMR time scale. Both *tert*-butyl isocyanide and phenyl isocyanide readily displace methyl isocyanide from **1** to produce $[Pd_2(CN\text{-}t\text{-}C_4H_9)_6](PF_6)_2$ and $[Pd_2(CNC_6H_5)_6](PF_6)_2$. Treatment of **1**, **2**, or **3** with triphenylphosphine in various ratios results in the isolation both mono- and bis(triphenylphosphine)-substituted complexes. Axial substitution by triphenylphosphine is preferred. The neutral complexes $Pd_2X_2(CNR)_4$ (X = I, R = CH_3, $t\text{-}C_4H_9$, C_6H_5; X = SCN, R = CH_3) are formed by refluxing $[Pd_2(CNR)_6](PF_6)_2$ with the halide or pseudohalide. These Pd(I) and Pt(I) complexes have been characterized by elemental analysis and infrared and proton magnetic resonance spectroscopy. Ionic complexes have also been characterized by solution conductivities. No reaction occurs between **1** and simple olefins or nitrogen donor ligands. Fluxional behavior has been found for $[Pd_2(CNCH_3)_6]^{2+}$ and $[Pd_2(CNCH_3)_5\{P(C_6H_5)_3\}]^{2+}$. These complexes have been studied in detail using line shape analysis techniques. The intramolecular rearrangement process for both molecules has been interpreted as involving a tetrahedral deformation about one metal center, rotation about the Pd–Pd bond, and a return to square-planar geometry. The activation parameters have been determined: for $[Pd_2(CNCH_3)_6]^{2+}$, $\Delta G^{\ddagger} = 13.2$ kcal/mol; for $[Pd_2(CNCH_3)_5\{P(C_6H_5)_3\}]^{2+}$, $\Delta G^{\ddagger} = 14.3$ kcal/mol.

Introduction

An increasing number of dimeric metal–metal bonded Pd(I) and Pt(I) complexes have been described within recent years.[1] Most of these M(I) species for which structural data are available contain bridging ligands. The preparation of the dimeric nonbridging isocyanide complexes **1**–**3** has been described recently.[2,3] A structural determination of the dipalladium complex **1** reveals two essentially square-planar



1, M = M' = Pd
2, M = M' = Pt
3, M = Pd, M' = Pt

coordination planes with a nearly perpendicular dihedral angle of 86.2° between them.[4] The Pd–Pd bond length of 2.531 Å is the shortest length reported for this bond. The diplatinum dimer **2** and the mixed-metal dimer **3** appear to have similar structures.[3]

Most previous studies of Pd(I) and Pt(I) complexes have been confined to the preparation and characterization of these species. However some substitution reactions of $Pd_2X_2(CN\text{-}t\text{-}C_4H_9)_4$ (X = Cl, Br, I) have been described,[11] and oxidation reactions of these complexes as well as of the dimers **1** and **3** have been reported.[11,3] This paper describes some substitution reactions of **1**–**3** with isocyanides, triphenylphosphine, halides, and pseudohalides. This portion of the work has been briefly reported[5] and some parallel observations by others have also recently appeared.[6] Preliminary studies have shown the dipalladium dimer **1** to be fluxional on the NMR time scale. A detailed study of the ^1H NMR line shapes of this complex as well as one of its triphenylphosphine substitution products, $[Pd_2(CNCH_3)_5\{P(C_6H_5)_3\}]^{2+}$, is also described.

Experimental Section

Preparation of Compounds. Methyl isocyanide[7] (*caution! toxic*), *tert*-butyl isocyanide,[8] phenyl isocyanide,[9] $Pd_2(DBA)_3{\cdot}CHCl_3$ (DBA = dibenzylideneacetone),[10] $Pd(CNC_6H_5)_2$,[11] $Pd(C_6H_5CN)_2Cl_2$,[12] $[Pd_2(CNCH_3)_6](PF_6)_2$,[3] $[Pt_2(CNCH_3)_6](BF_4)_2$,[3] and $[PdPt(CNCH_3)_6](PF_6)_2$,[3] were prepared by established procedures. Triphenylphosphine was recrystallized from benzene/ethanol. All other compounds were reagent grade and used without further purification.

$\mathbf{[Pd_2(CN\text{-}\mathit{t}\text{-}C_4H_9)_6](PF_6)_2}$. A solution of 300 mg of $[Pd_2(CNCH_3)_6](PF_6)_2$ and 0.4 ml of *tert*-butyl isocyanide in 10 ml of acetonitrile was heated at 90 °C for 5 min. An additional 0.2 ml of *tert*-butyl isocyanide was added and heating continued 5 min. The resulting solution was evaporated under vacuum. The white complex was recrystallized from hot 2-propanol; yield 81%. Anal. Calcd: C, 35.98; H, 5.43; N, 8.39. Found: C, 36.18; H, 5.28; N, 8.59.

$\mathbf{[Pd_2(CNC_6H_5)_6](PF_6)_2}$. Phenyl isocyanide (0.1 ml) was added to 108 mg of $[Pd_2(CNCH_3)_6](PF_6)_2$ in 15 ml of acetonitrile. The resulting solution was heated to reduce the volume to 8 ml. The product was precipitated by addition of diethyl ether to the solution. The white complex was recrystallized from acetone/ether; yield 77%. Anal. Calcd: C, 44.98; H, 2.70; N, 7.49. Found: C, 45.06; H, 2.67; N, 7.47.

$\mathbf{[Pd_2(CNCH_3)_5\{P(C_6H_5)_3\}](PF_6)_2}$. A solution of 35 mg (0.134 mmol) of triphenylphosphine in 3 ml of acetonitrile was added to 100 mg (0.134 mmol) of $[Pd_2(CNCH_3)_6](PF_6)_2$ in 4 ml of acetonitrile. The resulting solution was deep yellow. The yellow product was precipitated by the addition of 500 ml of diethyl ether. Purification was achieved by recrystallization from acetone/diethyl ether; yield 93%. Anal. Calcd: C, 34.66; H, 3.12; N, 7.22. Found: C, 34.80; H, 3.21; N, 7.16.

$\mathbf{[Pd_2(CNCH_3)_4\{P(C_6H_5)_3\}_2](PF_6)_2}$. This complex was prepared by the procedure described for $[Pd_2(CNCH_3)_5\{P(C_6H_5)_3\}](PF_6)_2$ using 70 mg (0.267 mmol) of triphenylphosphine and 100 mg (0.134 mmol) of $[Pd_2(CNCH_3)_6](PF_6)_2$ to obtain the bright yellow product; yield 86%. Anal. Calcd: C, 44.35; H, 3.55; N, 4.70. Found: C, 44.53; H, 3.47; N, 4.70.

$\mathbf{[PdPt(CNCH_3)_4\{P(C_6H_5)_3\}_2](PF_6)_2}$. A solution of 64.8 mg (0.247 mmol) of triphenylphosphine in 4 ml of acetonitrile was added to a solution of 103.5 mg (0.124 mmol) of $[PdPt(CNCH_3)_6](PF_6)_2$ in 6 ml of acetonitrile. The bright yellow solution was heated several minutes and the product reprecipitated by addition of diethyl ether. The solid was redissolved in 6 ml of acetonitrile and filtered into 55 ml of diethyl ether. The resulting cloudy mixture deposited thin yellow plates on standing for 4 h; yield 76%. Anal. Calcd: C, 41.28; H, 3.31; N, 4.38. Found: C, 41.1; H, 3.3; N, 4.7.

$\mathbf{[PdPt(CNCH_3)_5\{P(C_6H_5)_3\}](PF_6)_2}$. This pale yellow complex was prepared by the procedure described for $[PdPt(CNCH_3)_4\{P(C_6H_5)_3\}_2](PF_6)_2$ using 100 mg (0.119 mmol) of $[PdPt(CNCH_3)_6](PF_6)_2$ and 31.3 mg (0.119 mmol) of triphenylphosphine; yield 81%. Anal. Calcd: C, 31.76; H, 2.86; N, 6.61. Found: C, 32.63; H, 2.88; N, 6.54.

$\mathbf{[Pt_2(CNCH_3)_5\{P(C_6H_5)_3\}](BF_4)_2}$. A solution of 52.6 mg (0.201 mmol) of triphenylphosphine in 3 ml of acetonitrile was added to 162.8 ml (0.201 mmol) of $[Pt_2(CNCH_3)_6](BF_4)_2$ in 5 ml of acetonitrile. After heating of the resulting pale yellow solution for several minutes, the white complex was precipitated by the addition of diethyl ether and purified by recrystallization from acetonitrile/diethyl ether; yield 94%. Anal. Calcd: C, 32.61; H, 2.93; N, 6.79. Found: C, 32.5; H, 3.0; N, 6.6.

$\mathbf{Pd_2(CNCH_3)_4I_2}$. To a solution of 100 ml (0.134 mmol) of $[Pd_2(CNCH_3)_6](PF_6)_2$ in 15 ml of acetonitrile was added 60 mg (0.400 mmol) of sodium iodide. The resulting light orange mixture was heated for 5 min with swirling on a steam bath. After evaporation to dryness on a rotary evaporator, the solid was extracted with hot dichloromethane (6 × 15 ml). After being filtered, the orange solution was reduced in volume to 20 ml by heating. Recrystallization was achieved from either dichloromethane/hexane or slow evaporation of the dichloromethane solution to yield orange crystals; yield 81%. Anal. Calcd: C, 15.23; H, 1.92; N, 8.88. Found: C, 15.62; H, 2.06; N, 7.96.

$\mathbf{Pd_2(CN\text{-}\mathit{t}\text{-}C_4H_9)_4I_2}$. This complex was prepared from 60 mg (0.060 mmol) of $[Pd_2(CN\text{-}t\text{-}C_4H_9)_6](PF_6)_2$ and 36 mg (0.240 mmol) of sodium iodide by the procedure described for $Pd_2(CNCH_3)_4I_2$, except benzene was used for the extraction and recrystallization of the light orange product was effected by slow evaporation of a benzene solution; yield 79%. The infrared and ^1H NMR spectra were identical to those of the product obtained by a different route.[11] Anal. Calcd: C, 30.06; H, 4.54; N, 7.01. Found: C, 29.99; H, 4.45; N, 6.80.

$\mathbf{Pd_2(CNC_6H_5)_4I_2}$. **Method 1.** This light orange complex was prepared from 100 mg (0.089 mmol) of $[Pd_2(CNC_6H_5)_6](PF_6)_2$ and 40 mg (0.267 mmol) of sodium iodide by the procedure described for $Pd_2(CNCH_3)_4I_2$. Anal. Calcd: C, 38.25; H, 2.29; N, 6.37. Found: C, 37.72; H, 2.28; N, 6.14.

Method 2. $Pd(CNC_6H_5)_2I_2$ was prepared by refluxing a suspension of PdI_2 (1.0 g) and phenyl isocyanide (0.4 ml) in 20 ml of dichloromethane for 1 h. The orange solution was filtered and allowed to slowly evaporate, producing orange crystals of $Pd(CNC_6H_5)_2I_2$. Addition of a solution of 56.2 mg (0.099 mmol) of $Pd(CNC_6H_5)_2I_2$ in 10 ml of dichloromethane to 31 mg (0.099 mmol) of $Pd(CNC_6H_5)_2$ in 10 ml of dichloromethane resulted in formation of an orange solution. This solution was evaporated to dryness under vacuum and the product recrystallized from dichloromethane/diethyl ether. The product was identical with that produced by method 1.

$\mathbf{Pd_2(CNCH_3)_4(SCN)_2}$. This complex was prepared from 100 mg (0.134 mmol) of $[Pd_2(CNCH_3)_6](PF_6)_2$ and 40 mg (0.412 mmol) of potassium thiocyanate by the procedure described for $Pd_2(CNCH_3)_4I_2$; yield 77%. Anal. Calcd: C, 24.25; H, 2.05; N, 17.11. Found: C, 24.08; H, 2.05; N, 16.70.

$\mathbf{[Pd(CNCH_3)_2\{P(C_6H_5)_3\}_2](PF_6)_2}$. A solution of 93.6 mg (0.357 mmol) of triphenylphosphine in 5 ml of acetonitrile was added to 100 mg (0.178 mmol) of $[Pd(CNCH_3)_4](PF_6)_2$ in 5 ml of acetonitrile. After evaporation to reduce the volume to 5 ml, the product was precipitated by the addition of diethyl ether. The white complex was recrystallized from acetone/diethyl ether; yield 90%. Anal. Calcd: C, 47.90; H, 3.62; N, 2.79. Found: C, 47.41; H, 3.59; N, 2.82.

Physical Measurements. Conductivities were determined over a range of concentrations in nitromethane solution using an Industrial Instruments conductivity bridge. The slopes *B* of the straight-line plots of the difference in conductivity at infinite dilution and the equivalent conductivity vs. the square root of the equivalent concentration were derived according to the method of Feltham and Hayter.[13] For otherwise similar complexes, the slope *B* is a useful indicator of the charge type (Table I). Infrared spectra were recorded on a Beckman IR-12 spectrophotometer. Proton magnetic resonance spectra were recorded on a JEOL JNM-MH-100 spectrometer operating at 100 MHz.

Variable-Temperature ^{1}H NMR Studies. Variable-temperature experiments were performed with the JEOL spectrometer and ancillary

Table I. Conductivity Data

Compd	B^a	Charge type
$[Pd_2(CN\text{-}t\text{-}C_4H_9)_6](PF_6)_2$	265	2:1
$[Pd_2(CNC_6H_5)_6](PF_6)_2$	322	2:1
$[Pd_2(CNCH_3)_5\{P(C_6H_5)_3\}](PF_6)_2$	301	2:1
$[Pd_2(CNCH_3)_4\{P(C_6H_5)_3\}_2](PF_6)_2$	262	2:1
$[PdPt(CNCH_3)_5\{P(C_6H_5)_3\}](PF_6)_2$	282	2:1
$[PdPt(CNCH_3)_4\{P(C_6H_5)_3\}_2](PF_6)_2$	272	2:1
$[Pt_2(CNCH_3)_5\{P(C_6H_5)_3\}](BF_4)_2$	312	2:1
$[Pd_2(CNCH_3)_6](PF_6)_2{}^b$	256	2:1
$[Au\{C(NHCH_3)_2\}_2](PF_6)^c$	151	1:1

[a] In $cm^{1/2}$ $equiv^{-1/2}$ Ω^{-1}. [b] See ref 2. [c] J. E. Parks and A. L. Balch, *J. Organomet. Chem.*, 71, 456 (1974).

JES-VT-3 temperature controller. Probe temperatures were monitored by means of a thermocouple calibrated against standard methanol and ethylene glycol samples. At least 5 min was allowed at each temperature to ensure thermal equilibrium. The field homogeniety was maximized between scans to offset deterioration in signal due to instrumental instability and temperature changes. A version of Whiteside's EXCNMR multisite exchange program was modified to run on the Burroughs B6700 computer at the University of California, Davis, Calif. Kubo–Sack exchange matrices were derived using the method of Johnson and Moreland.[14] Other input parameters were obtained from the low-temperature limit experimental spectra. Below the coalescence point, experimental spectra were matched to calculate spectra using the ratio of maximum peak intensities to minimum central intensity, the full line width at half-maximum amplitude, and visual inspection of the line shapes. Below coalescence, spectra were fitted using the full line width at half-height and visual inspection. See Table II for spectral data.

Arrhenius activation energies, E_a, and frequency factors, A, were obtained in the usual manner from the slope and intercept of the least-squares straight-line plots of log k vs. $1/T$, where $k = 1/\tau$ is the first-order rate constant for the exchange. The free energy of activation, $\Delta G^{\ddagger}$ was calculated from

$$k = (k_B T/h)\exp(-\Delta G^{\ddagger}/RT)$$

where k_B is Boltzmann's constant and h is Planck's constant.

Errors in the activation parameters were calculated by[15]

$$\sigma_{\Delta G^{\ddagger}} = \{[\ln(k_B T/hk)]^{-2}(\sigma_k/k)^2 + (\sigma_T/T)^2\}^{1/2}\Delta G^{\ddagger}$$

$$\sigma_{E_a} = \{[2T^2/(\Delta T)^2](\sigma_T/T)^2 + 2[\Delta(\ln k)]^{-2}(\sigma_k/k)^2\}^{1/2}E_a$$

The error in T was taken as 2 °C and the error in k as 50% of the value of k.

Results and Discussion

Isocyanide Substitution. Ligand exchange between free methyl isocyanide and either **1** or **2** is fast on an NMR time scale. Spectra of solutions of **1** below −8 °C or **2** at room temperature without free isocyanide exhibit peaks due to both axial and equatorial isocyanide ligands. Addition of free methyl isocyanide to these solutions gives spectra with only a single averaged peak. In the case of **1** the peak remains unsplit at temperatures as low as −50 °C. Treatment of **1** with an excess of either *tert*-butyl isocyanide or phenyl isocyanide results in complete displacement of methyl isocyanide and the formation of $[Pd_2(CN\text{-}t\text{-}C_4H_9)_6](PF_6)_2$, **4**, and $[Pd_2(CNC_6H_5)_6](PF_6)_2$, **5**. This reaction is performed in a boiling acetonitrile solution so that the volatile methyl isocyanide is allowed to escape as vapor. The infrared spectra of **4** and **5** indicate that only terminal isocyanide ligands are present. The ^1H NMR spectrum of **4** exhibits a singlet at τ 8.39 in acetone-d_6, while the spectrum of **5** consists of a complex multiplet centered at τ 2.2. Neither complex contains any trace of methyl isocyanide. The ^1H NMR spectrum of **4** in acetone solution has been studied as a function of temperature from +40 to −85 °C; only a single peak is observed at all temperatures.

Triphenylphosphine Substitution. Triphenylphosphine reacts with solutions of **1**, **2**, or **3** in acetone or acetonitrile to yield crystalline substitution products. Addition of 1 mol of triphenylphosphine to **1** produces $[Pd_2(CNCH_3)_5\{P(C_6H_5)_3\}](PF_6)_2$, **6**. The infrared spectrum of this product indicates that only terminal isocyanide ligands are present. The ^1H NMR spectrum of the methyl region of **6** in acetone-d_6 below −8 °C consists of three resonances at τ 6.37, 6.29, and 6.54 (relative intensities 1:2:2). The only formulation consistent with these results is a structure in which the bulky triphenylphosphine ligand occupies an axial position. Addition of 2 or more mol of triphenylphosphine to **1** produces the disubstituted complex $[Pd_2(CNCH_3)_4\{P(C_6H_5)_3\}_2](PF_6)_2$, **7**. The ^1H NMR spectrum of **7** in acetone-d_6 solution consists of a single methyl resonance at τ 6.60, which shifts slightly over the temperature range −84 to +50 °C but remains unsplit. The appearance of such a simple spectrum for **7** indicates that the triphenylphosphine ligands preferentially occupy axial positions. In order to ensure that **6** and **7** were true Pd(I) complexes and not Pd(II) complexes, triphenylphosphine

Table II. Infrared and ^1H NMR Spectral Data

	IR[a]	^1H NMR			
Compd	ν_{CN}, cm^{-1}	Assignment	τ (intens)[b]	Coupling	Solvent
$[Pd_2(CN\text{-}t\text{-}C_4H_9)_6](PF_6)_2$	2200	$(CH_3)_3CNC$	8.38 (54)	None	$(CD_3)_2CO$
$[Pd_2(CNC_6H_5)_6](PF_6)_2$	2190	C_6H_5NC	2.0–2.4 (30)[c]		$(CD_3)_2CO$
$[Pd_2(CNCH_3)_5\{P(C_6H_5)_3\}](PF_6)_2$	2232	CH_3NC	6.54 (6)	None	$(CD_3)_2CO^d$
		CH_3NC	6.37 (3)	None	
		CH_3NC	6.29 (6)	None	
		$P(C_6H_5)_3$	2.32 (15)[c]		
$[Pd_2(CNCH_3)_4\{P(C_6H_5)_3\}_2](PF_6)_2$	2220	CH_3NC	6.60 (12)	None	$(CD_3)_2CO$
		$P(C_6H_5)_3$	2.41 (30)[c]		
$[Pd(CNCH_3)_2\{P(C_6H_5)_3\}_2](PF_6)_2$	2272	CH_3NC	7.29 (6)	None	CD_3CN
		$P(C_6H_5)_3$	2.35 (30)	None	
$[PdPt(CNCH_3)_5\{P(C_6H_5)_3\}](PF_6)_2$	2238	CH_3NC	6.35–6.95 (15)[c]		CD_3CN
		$P(C_6H_5)_3$	2.32 (15)	None	
$[PdPt(CNCH_3)_4\{P(C_6H_5)_3\}_2](PF_6)_2$	2221	CH_3NC	6.59 (6)	$^4J_{Pt-H} = 16.1$ Hz	CD_3CN
		CH_3NC	6.56 (6)	$^5J_{Pt-H} = 2.8$ Hz	
		$P(C_6H_5)_3$	2.34 (30)[c]		
$[Pt_2(CNCH_3)_5\{P(C_6H_5)_3\}](BF_4)_2$	2238	CH_3NC	6.3–6.9 (15)[c]		CD_3CN
		$P(C_6H_5)$	2.35 (15)[c]		
$Pd_2(CNCH_3)_4I_2$	2212	CH_3NC	6.56 (12)	None	$CDCl_3$
$Pd_2(CNC_6H_5)_4I_2$	2165	C_6H_5NC	2.55 (20)	None	$CDCl_3$
$Pd_2(CNCH_3)_4(SCN)_2$	2217	CH_3NC	6.53 (12)	None	CD_3CN
$Pd_2(CNCH_3)_4Cl_2$	2218	CH_3NC	6.56 (12)	None	$CDCl_3$

[a] Fluorocarbon mulls. [b] Relative peak intensities normalized to proton counts consistent with specific structural assignments. [c] Complex multiplet. [d] Data below −8 °C.

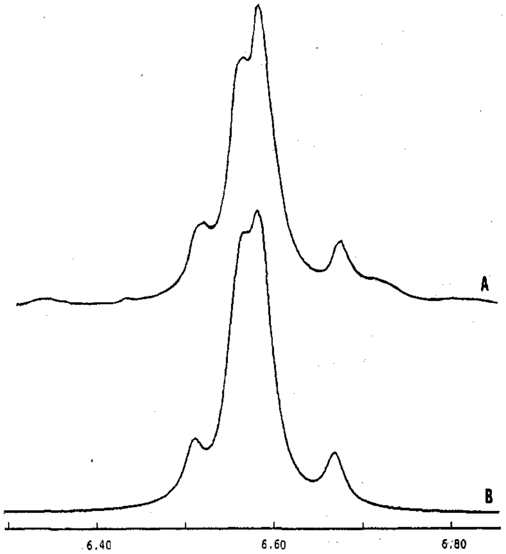
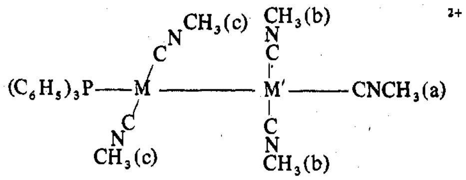
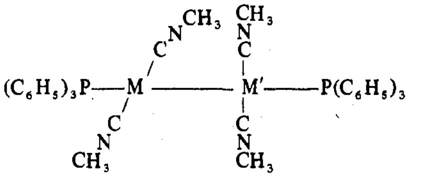


Figure 1. ^{1}H NMR spectra for the methyl region of $[PdPt(CNCH_3)_4\{P(C_6H_5)_3\}_2](PF_6)_2$ in acetonitrile-d_3 at 30 °C: A, experimental; B, calculated.



6, M = M' = Pd
8, M = Pd, M' = Pt
10, M = M' = Pt



7, M = M' = Pd
9, M = Pd, M' = Pt

substitution of $Pd(CNCH_3)_4^{2+}$ was examined. Regardless of the ratio of triphenylphosphine to $Pd(CNCH_3)_4^{2+}$, only one substitution product—the colorless, disubstitution product $[Pd(CNCH_3)_2\{P(C_6H_5)_3\}_2](PF_6)_2$—could be obtained. The infrared and ^{1}H NMR spectra of this complex indicate that it is a normal planar Pd(II) complex probably with trans geometry.

The reaction of $[PdPt(CNCH_3)_6](PF_6)_2$ with triphenylphosphine in a 1:1 or 1:2 ratio produces mono- and bis(triphenylphosphine)-substituted complexes, respectively. The ^{1}H NMR spectrum of $[PdPt(CNCH_3)_4\{P(C_6H_5)_3\}_2](PF_6)_2$, **9**, in the methyl region consists of two triplets with 1:4:1 intensity ratios and splittings of 16.1 and 2.8 Hz (Figure 1). The structure is similar to that of **7**, with both axial positions substituted by triphenylphosphine. The triplet with the larger splitting is assigned to the equatorial isocyanide bound to platinum ($^4J_{Pt-H} = 16.1$ Hz) while the other triplet is assigned to the equatorial isocyanides bound to palladium ($^5J_{Pt-H} = 2.8$ Hz). Since the resolution of this latter triplet did not allow determination of the coupling constant directly from the experimental spectrum, this splitting was derived from the closest fit of a calculated spectrum to the experimental. The assignments of $^4J_{Pt-H}$ and $^5J_{Pt-H}$ are made on the assumption that $^4J_{Pt-H}$ is larger than $^5J_{Pt-H}$. Since this relation need not necessarily hold, it is possible that the assignments might be reversed. The structure of the monosubstituted complex, $[PdPt(CNCH_3)_5\{P(C_6H_5)_3\}](PF_6)_2$, **8**, cannot be assigned with certainty. Physical characterization data, including the correct triphenylphosphine:methyl isocyanide ratio from the ^{1}H NMR spectrum, confirm the molecular formula. Additionally, the ^{1}H NMR peak shifts and splittings in the methyl region show that neither **3** nor **9** is present. The ^{1}H NMR spectrum of the methyl region of **8** in acetonitrile-d_3 shows a complex set of splittings and overlapping peaks at τ 6.35–6.95. The most reasonable explanation of these data is a mixture of the two axially substituted dimers, with triphenylphosphine bound to either a palladium atom or a platinum atom. Triphenylphosphine substitution in an equatorial position also cannot be ruled out in this case.

Triphenylphosphine substitution also occurs with complex **2**. Reaction in a 1:1 ratio leads to the formation of $[Pt_2(CNCH_3)_5\{P(C_6H_5)_3\}](BF_4)_2$, **10**. This complex has been characterized by infrared (ν_{CN} 2238 cm^{-1}) and ^{1}H NMR (triphenylphosphine:methyl isocyanide = 1:5) spectroscopy and by elemental analysis and conductivity. The ^{1}H NMR spectrum of the methyl region of **10** is complex and has not been amenable to interpretation. No trace of the unreacted dimer **2** is present. It is probable that a mixture of axially and equatorially substituted dimers occurs. No attempts have been made to separate the possible isomers of either **8** or **10**.

Halide and Pseudohalide Substitution. The complexes $Pd_2(CN\text{-}t\text{-}C_4H_9)X_2$ (X = Cl, Br, I) have been synthesized previously[11] by the reaction of the difficultly obtained[16] "$Pd(CN\text{-}t\text{-}C_4H_9)_2$" with $PdX_2(CN\text{-}t\text{-}C_4H_9)_2$ under an inert atmosphere. Some complexes of this type are also readily prepared by addition of halide or pseudohalide to $[Pd_2(CNR)_6]^{2+}$.

Addition of excess sodium iodide to an acetonitrile solution containing $[Pd_2(CN\text{-}t\text{-}C_4H_9)_6](PF_6)_2$ followed by a short reflux produces $Pd_2(CN\text{-}t\text{-}C_4H_9)_4I_2$ in high yield. After evaporation of the acetonitrile solution, the product may be separated from sodium hexafluorophosphate and excess sodium iodide by extraction with benzene. $Pd_2(CN\text{-}t\text{-}C_4H_9)_4I_2$ obtained in this manner is identical with the product previously obtained by Otsuka and co-workers.[11] This reaction has been extended to include other isocyanide dimers. Thus, both $[Pd_2(CNCH_3)_6](PF_6)_2$ and $[Pd_2(CNC_6H_5)_6](PF_6)_2$ react with sodium iodide to yield $Pd_2(CNCH_3)_4I_2$ and $Pd_2(CNC_6H_5)_4I_2$, respectively. Reactions with other halides and pseudohalides have also been attempted. Potassium thiocyanate reacts with **1** to produce $Pd_2(CNCH_3)_4(SCN)_2$. Addition of either sodium cyanide or sodium azide to **1** in acetonitrile solution produces decomposition with the formation of uncharacterized black solids. Sodium chloride does not react with **1**, while sodium bromide reacts to only a small extent. The infrared spectrum of the product from the bromide reaction consists mainly of peaks due to unreacted **1**, but a small shoulder at 2222 cm^{-1} indicates the formation of some $Pd_2(CNCH_3)_4Br_2$. The reactivity order of the halides is consistent with other observations of these complexes. When **1** was synthesized by the spontaneous reduction of $Pd(CNCH_3)_4^{2+}$ in aqueous solution, a large concentration of chloride ion was present, yet only **1** and no $Pd_2Cl_2(CNMe)_4$ was observed to form.[3] Chloride is simply too weak a nucleophile to displace an isocyanide ligand from **1** under these conditions. Additionally it has been reported that $Pd_2X_2(CNCH_3)_4$ (X = Cl or Br) will react with methyl isocyanide to give the chloride or bromide salts of **1**.[6]

These halide and pseudohalide complexes have been characterized by infrared and ^{1}H NMR spectroscopy and by satisfactory elemental analysis. In all cases, the isocyanide stretching frequency of the parent dimer is replaced by a new, slightly lower stretching frequency for the neutral product. Additionally, the strong, broad band near 840 cm^{-1} due to the phosphorus–fluorine stretch vanishes. The ^{1}H NMR spectra of all of these complexes exhibit a single peak, which is assigned to the protons of the isocyanide ligand. A conductivity determination in nitromethane solution of $Pd_2(CNCH_3)_4Cl_2$ showed it to be a nonelectrolyte. With the exception of $Pd_2(CNCH_3)_4I_2$, these complexes show good air and thermal stability. $Pd_2(CNCH_3)_4I_2$ disproportionates into $Pd(CNCH_3)_2I_2$ and presumably Pd(0) species at elevated temperatures. Disproportionation also occurs more slowly in solution at room temperature.

The structures of these complexes are uncertain. Otsuka et al.[11] have postulated structures with bridging halides, based on the low-frequency infrared spectra and lack of absorptions in the bridging isocyanide region. Bridging isocyanides may be ruled out with certainty, but as pointed out elsewhere[6] the interpretation of the low-energy infrared spectrum of these dimers is not clear. The complexes almost certainly have planar geometry about each metal but the presence or absence of bridging anions remains to be established.

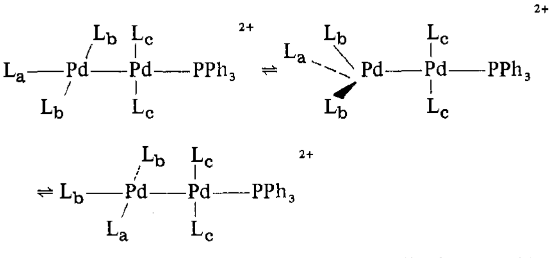
Other Attempted Reactions. Experiments have shown that **1** is unreactive toward a number of potential reactants. Treatment of **1** in acetonitrile with carbon monoxide at 1 atm produces no reaction. Pyridine, 2,2′-bipyridine, and 2,2′,2″-terpyridine do not react with **1**. No reaction of **1** with olefins has been detected. Refluxing **1** in acetone solution with an excess of 1,5-cyclooctadiene, acrylonitrile, or tetrachloroethylene produces no new products. After treatment with **1** (acetonitrile solution, 50 °C, up to 6 days) no isomerization of 1,3-cyclooctadiene, 1,5-cyclooctadiene, or 1-octene was detected.

Dynamic Nuclear Magnetic Resonance Studies. Several of the complexes characterized in this and previous work have been found to exhibit fluxional behavior on the NMR time scale. Two of these complexes, $[Pd_2(CNCH_3)_5\{P(C_6H_5)_3\}](PF_6)_2$ and $[Pd_2(CNCH_3)_6](PF_6)_2$, have been studied in detail using computer-generated line analysis techniques. The ^1H NMR spectrum of **6** in acetone-d_6 solution below –8 °C contains three methyl resonances at τ 6.37, 6.39, and 6.54 with relative intensity ratios of 1:2:2. On the basis of the temperature dependence of this spectrum which is shown in Figure 2, these resonances are assigned to the groups of **6** labeled a, b, and c respectively. Above –8 °C, the resonances assigned to groups a and b broaden, coalesce at –3 °C, and narrow on further heating. The resonance for group c remains unperturbed. Further heating to +40 °C does not alter the spectrum. Upon cooling, the ^1H NMR observations are reversed. Somewhat above +40 °C, decomposition of the complex begins to rapidly occur, resulting in the formation of black solids and the loss of the previously observed spectrum into one broad peak. Varying traces of free methyl isocyanide have been found in different preparations of **6**. This free isocyanide exchanges rapidly with coordinated isocyanide probably through an associative process. Reproducible coalescence temperatures cannot be obtained unless small amounts (ca. 5 mg) of solid palladium chloride are added to the NMR tube.[17] Palladium chloride scavenges free methyl isocyanide and samples treated in this manner allow reproducible spectra to be obtained. The temperature dependence of the spectrum of **6** in the absence of free methyl isocyanide is not affected by concentration changes. Dilution of the original solution by half does not change the observations. Thus, the exchange mechanism in the absence of free methyl isocyanide must be intraionic. A mechanism involving bridging isocyanides does not appear reasonable since this should equilibrate isocyanide ligands between both metals. A process creating tetrahedral geometry at the palladium atom containing groups a and b and allowing free rotation about the Pd–Pd bond is sufficient to account for the observations. One cycle of such a process is shown in eq 1. The transition state in this process can be conveniently described as a Pd(0)–Pd(II) species with tetrahedral geometry at Pd(0) and planar geometry at Pd(II). Achieving such a state requires merely an alteration of charge distribution in the ground state.

Table III. Dynamic ^1H NMR Thermodynamic Parameters

	$[Pd_2(CNCH_3)_6](PF_6)_2$	$[Pd_2(CNCH_3)_5\{P(C_6H_5)_3\}](PF_6)_2$[a]
Coalescence temp, °C	–8	–4
E_a, kcal/mol	13.8	15.6
σ_{E_a}, kcal/mol	1.4	3.7
log A	13.2	13.7
$\Delta G^{\ddagger}$,[a] kcal/mol	13.2	14.3
$\sigma_{\Delta G^{\ddagger}}$, kcal/mol	0.3	0.3

[a] At the coalescence temperature.



(1)

The temperature dependence of the ^1H NMR spectrum of **1** has been briefly described before.[2,3] At temperatures below –14 °C two resonance at τ 6.25 and 6.33 of relative intensity ratio 2:1 are observed. This is consistent with the solid-state structure which showed two isocyanides in different ligand environments.[3] Above –14 °C the resonances broaden, coalesce at –80 °C, and narrow above +4 °C to give a single peak. Once again, concentration effects do not alter the spectra when palladium chloride is added to scavenge any free isocyanide. Three plausible mechanisms have been postulated for the rearrangement process.[2] The first, similar to that found for **6**, involves a tetrahedral distortion about a Pd(I) center, rotation about the Pd–Pd bond, and a return to square–planar geometry. The second process involves simultaneous tetrahedral distortions about both Pd atoms, rearrangement, and a return to square-planar geometry. The third process involves ligand exchange between metal centers via bridging isocyanides. On the basis of the observations on **6** this latter process appears unlikely.

Complete line shape calculations for **6** were performed based on the rearrangement process defined by eq 1. Similar calculations were also performed for **1**. The rate (k) is defined as the inverse of the mean lifetime (τ) between the deformation of original configuration and a return to square-planar geometry. Values of τ for the two-site exchange process were obtained by comparing experimental spectra with the computed spectra. A comparison of these spectra is shown in Figures 2 and 3. Arrhenius activation parameters, E_a and A, and the free energies of activation at the coalescence temperatures, $\Delta G^{\ddagger}$, are listed in Table III. For **6** the protons of the group c methyl isocyanide ligands were also included in the computed spectra, though they do not exchange. Due to the fact that these protons are coupled to the isocyanide nitrogen ($I = 1$), these protons are split into a triplet of equally intense peaks. This coupling is usually eliminated due to quadrupolar relaxation but is observed in some isocyanides.[18] The protons of **1** and of groups a and b of **6** are not split by this coupling.

The activation parameters for **1** and **6** are comparable. In contrast the ^1H NMR spectrum of the platinum dimer **2** is invariant over the temperature range 20–140 °C.[3] On the basis of the peak separations and the lack of line broadening at 140 °C for **2** we can set a very conservative lower limit of 21 kcal/mol for $\Delta G^{\ddagger}$ for intraionic axial–equatorial interchange

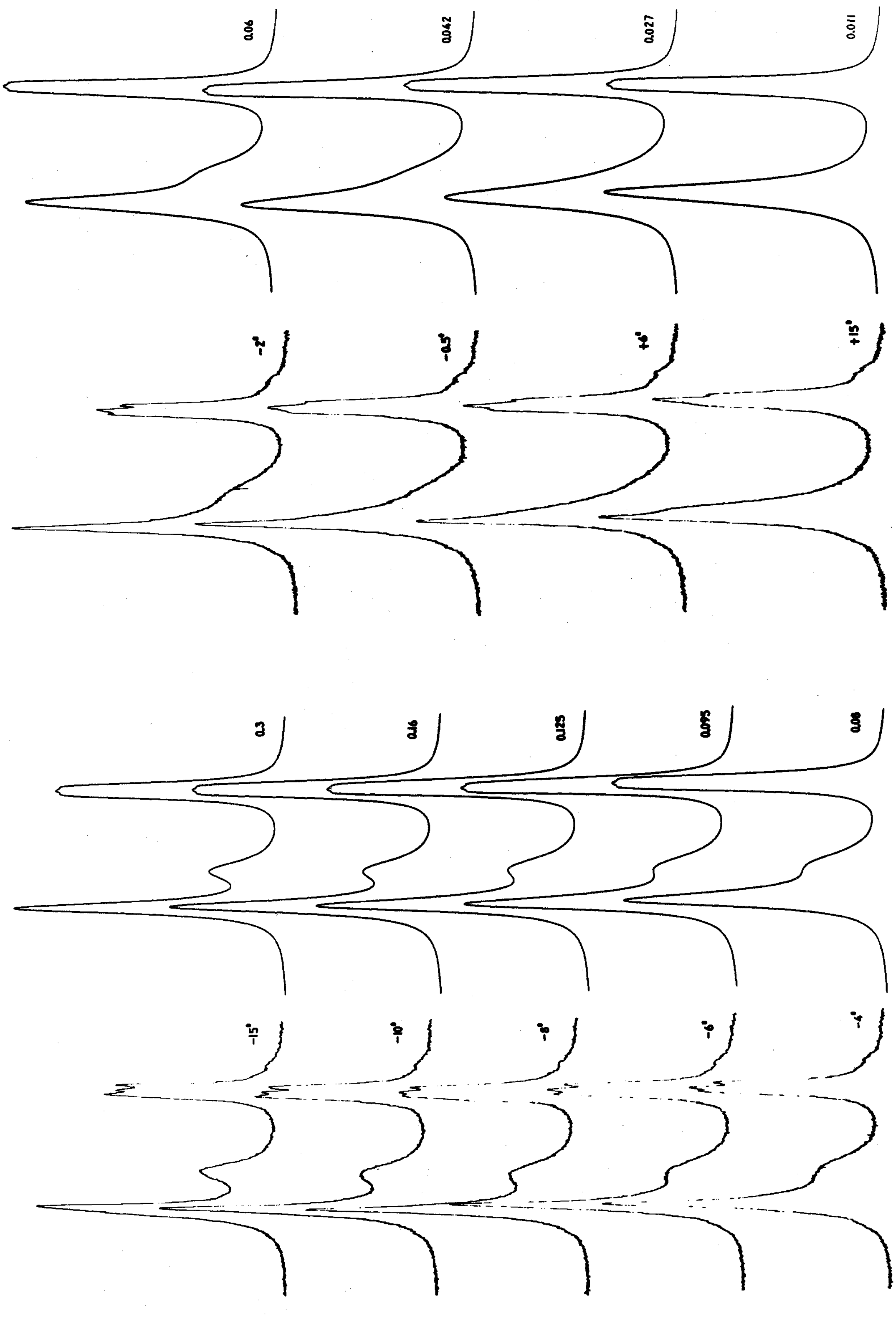


Figure 2. ^{1}H NMR spectra of the methyl region of $[Pd_2(CNCH_3)_5\{P(C_6H_5)_3\}](PF_6)_2$ in acetone-d_6 as a function of temperature. Calculated spectra are shown to the right of each matching experimental spectrum. The lifetime (τ) values for each calculated spectrum are given in seconds.

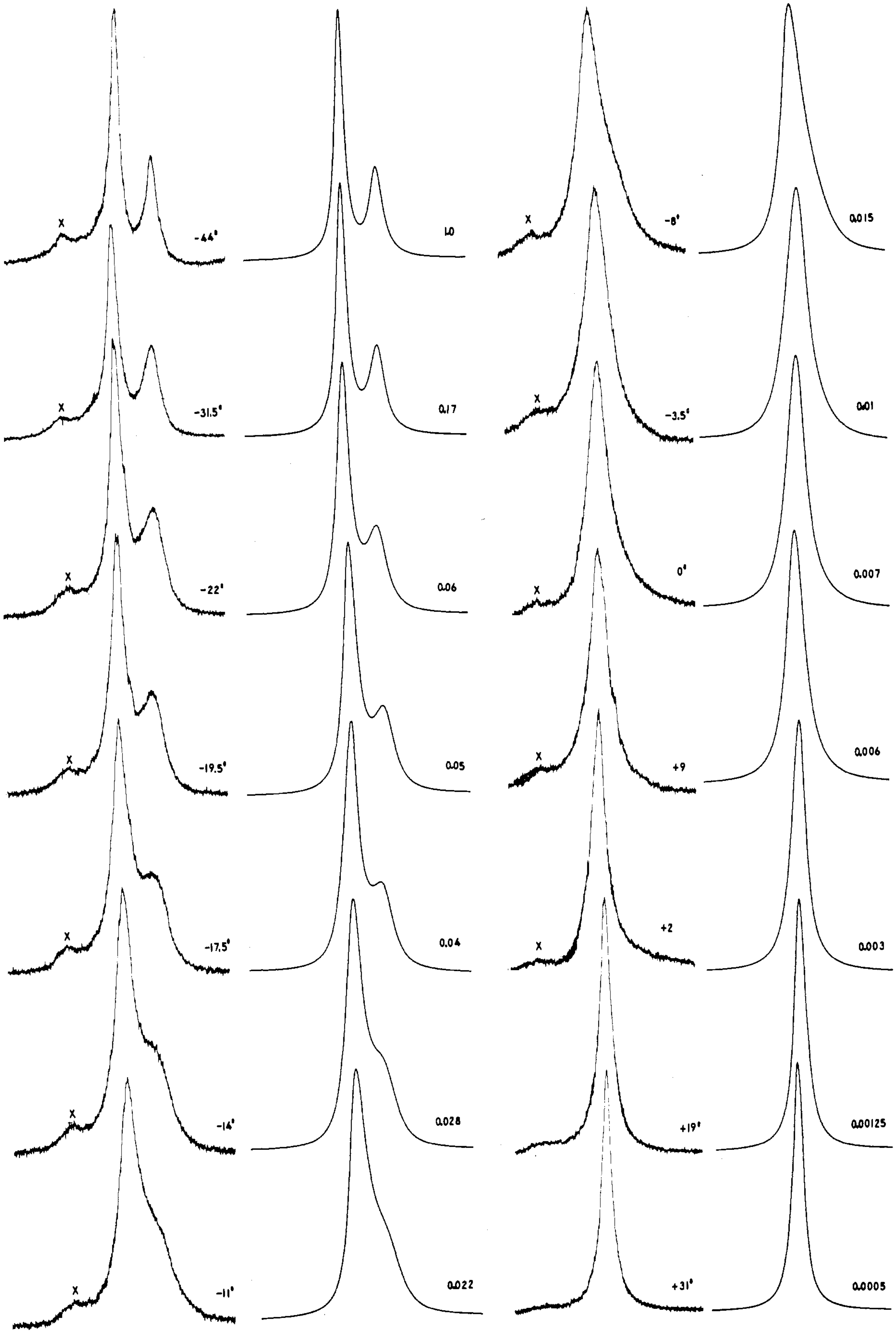


Figure 3. ${}^1H$ NMR spectra for $[Pd_2(CNCH_3)_6](PF_6)_2$ in acetone-d_6 as a function of temperature. Calculated spectra are shown to the right of each matching experimental spectrum. The lifetime (τ) values for each calculated spectrum are given in seconds. The peaks marked "X" are due to an impurity in the sample.

in **2**. However we must emphasize that there is no evidence even at 140 °C that any axial–equatoral exchange occurs in **2**. Moreover since couplings of the methyl isocyanide protons to two different platinum atoms are observed in **2** even at 140 °C, exchange of isocyanide ligands between the two metals is also ruled out in this complex. In most cases where barriers to rearrangement processes at a metal center have been measured it has been noted that the barrier for a third-row transition metal is larger than for a second-row metal.[19] However in the present case where **1** and **2** are compared, the difference in barrier height between these two is more striking than usual.

Acknowledgment. We thank Matthey Bishop for a generous loan of platinum salts and the National Institutes of Health for support.

Registry No. $[Pd_2(CN\text{-}t\text{-}C_4H_9)_6](PF_6)_2$, 59561-00-1; $[Pd_2(CNC_6H_5)_6](PF_6)_2$, 60039-64-7; $[Pd_2(CNCH_3)_5\{P(C_6H_5)_2\}](PF_6)_2$, 60039-66-9; $[Pd_2(CNCH_3)_4\{P(C_6H_5)_3\}_2](PF_6)_2$, 60125-83-9; $[Pd(CNCH_3)_2\{P(C_6H_5)_3\}_2](PF_6)_2$, 61258-88-6; $[PdPt(CNCH_3)_5\{P(C_6H_5)_3\}](PF_6)_2$, 61288-82-2; $[PdPt(CNCH_3)_4\{P(C_6H_5)_3\}_2](PF_6)_2$, 60125-87-3; $[Pt_2(CNCH_3)_5\{P(C_6H_5)_3\}](BF_4)_2$, 60039-68-1; $Pd_2(CNCH_3)_4I_2$, 61258-82-0; $Pd_2(CNC_6H_5)_4I_2$, 61258-85-3; $Pd_2(CNCH_3)_4(SCN)_2$, 61258-83-1; $Pd_2(CNCH_3)_4Cl_2$, 61258-81-9; $Pd_2(CN\text{-}t\text{-}C_4H_9)_4I_2$, 61258-84-2; $[Pd_2(CNCH_3)_6](PF_6)_2$, 56116-48-4; $[PdPt(CNCH_3)_6](PF_6)_2$, 60767-38-6; $[Pt_2(CNCH_3)_6](BF_4)_2$, 60767-37-5; $[Pd(CNCH_3)_4](PF_6)_2$, 38317-62-3; $Pd(CNC_6H_5)_2$, 41021-81-2; $Pd(CNCH_5)_2I_2$, 61302-31-6.

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Contribution from Istituto di Chimica Fisica, Universita di Messina, Messina, Italy,
and the William Ramsay and Ralph Forster Laboratories, University College, London, W.C.1, England

Kinetics of the Chelate Effect. Ring Closing and Ring Opening in *cis*-Dichloro(dimethyl sulfoxido)(2-aminoethylammonium)platinum(II) Chloride

RAFFAELE ROMEO, SANTO LANZA, and MARTIN L. TOBE*

Received September 3, 1976 AIC606573

The kinetics of the reaction *cis*-$[Pt(dmso)(enH)Cl_2]^+ \rightleftarrows [Pt(dmso)(en)Cl]^+ + H^+ + Cl^-$ (dmso = S-bonded dimethyl sulfoxide, enH = monodentate 2-aminoethylammonium, and en = 1,2-diaminoethane) have been studied in both directions in aqueous solution at 30.0 °C, $\mu = 2.0$ ($LiClO_4$). The specific rate constant for the approach to equilibrium, k_{obsd}, is given by the expression $k_{obsd} = (k^f{}_{Cl}K_a'[Cl^-] + k^f{}_{H_2O}K_a''K_{Cl})[H^+]^{-1}([Cl^-] + K_{Cl})^{-1} + k^r{}_{Cl}[Cl^-]$. This is interpreted in terms of a rapid equilibrium between the chloro and aquo open-chain species (chloride trans to dmso), equilibrium constant $K_{Cl} = 6.2 \times 10^{-4}$ M, and rapid acid–base equilibria between these complexes and their reactive bases (equilibrium constants K_a' and K_a'', respectively) which undergo first-order ring closure with rate constants $k^f{}_{Cl}$ and $k^f{}_{H_2O}$, respectively; $k^f{}_{Cl}K_a' = 1.50 \times 10^{-4}\ M^{-1}\ s^{-1}$ and $k^f{}_{H_2O}K_a'' = 5.91 \times 10^{-3}\ M^{-1}\ s^{-1}$. The second-order rate constant for ring opening, $k^r{}_{Cl} = 1.0 \times 10^{-4}\ M^{-1}\ s^{-1}$. This behavior is compared to that of an analogous system involving two monodentate cyclohexylamine ligands and the consequences of chelation are examined.

Introduction

The study of the chelate effect has a long history in the field of complex formation equilibrium constants[1] and from time to time attempts have been made to investigate the chelate effect from a kinetic point of view by measuring the rates of ring opening and ring closing. Much of the published work relates to octahedral complexes where the substitution is generally dissociatively activated and an examination of the chelate effect would have to include an analysis of the rate of ring closure in terms of effective aggregate formation constants in an I_d mechanism or competition for five-coordinate intermediates in a D mechanism.[2-4] For associatively activated systems the kinetics of ring closing and ring opening can, in principle, be analyzed much more easily in terms of rate constants and the active participation of the solvent in either solvolytic or anation processes can be bypassed. Many studies have now been made of the kinetics of ring closing in square-planar systems, some superficial and some in con-

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* To whom correspondence should be addressed at University College.